

Kelly et al.
Serial No. 09/759,920
Amendment

Page two

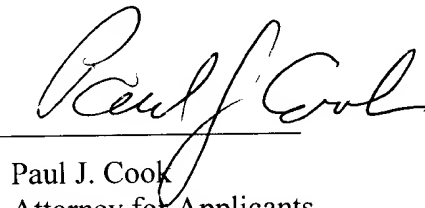
regarding IEP in the provisional application. Accordingly, it is submitted that the provisional application provides adequate support for Claims 3, 4, 9 and 10.

Claim 31 has been rejected under 35 USC 112 for failing to define pore diameter. Claim 31 has been amended to correct this error. Accordingly, this ground of rejection should be withdrawn.

In view of the above, it is submitted that applicants' claims define allowable subject matter and a Notice of Allowance is respectfully requested.

Respectfully submitted,

By



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MARKED UP CLAIMS

31. (Twice Amended) The filter of Claim 1 wherein one or more porous filters have a nominal pore diameter between 0.1 and 1 micron.

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Posted on: 03/01/2002

Measuring Zeta Potential

By Richard O'Brien, Ph.D., Director of Research & Development, Colloidal Dynamics, Eveleigh, Australia; and Russell Mann, Sales Manager, Colloidal Dynamics, Warw R.I.

A new instrument provides rapid and accurate measurements of zeta potential without the need for sample preparation.

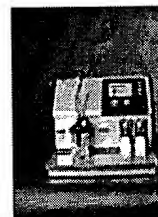
Important ceramic processes, such as slip casting, require stable, well-dispersed colloidal suspensions to achieve optimal casting behavior and green body properties. Colloidal particles are nearly always electrically charged. If the charge is high enough, the electrical repulsive forces will stop the particles from agglomerating, and stable suspensions with low relative viscosity can be prepared.

The particle charge can be manipulated and controlled by adjusting the suspension pH and by using suitable dispersants, such as polyelectrolytes. However, optimizing the formulation of these materials requires a suitable method for measuring the particle charge, known as the zeta potential.

A new device* has been developed that provides rapid and accurate measurements of zeta potential without the need for sample preparation. The analyzer makes direct measurements on samples over a very wide concentration range, including the high concentrations used in ceramic slips. The instrument can handle samples ranging from flowing fluids to flocculated pastes and gels. A key feature of the product is its automatic titration capabilities for measuring zeta potential versus pH or as a function of dispersion concentration.

The Importance of Zeta Potential

The charge on colloidal particles can arise from a number of different mechanisms, including dissociation of acidic or basic groups on the particle surface, or adsorption of a charged



The new Zeta allows zeta potential measurements made over a particle concentration range.

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species from solution. The particle charge is balanced by an equal and opposite charge carried by ions in the surrounding liquid. These counter ions tend to cluster around the particles in diffuse clouds. This arrangement of particle surface charge surrounded by a diffuse cloud of countercharge is called the electrical double layer (see Figure 1).

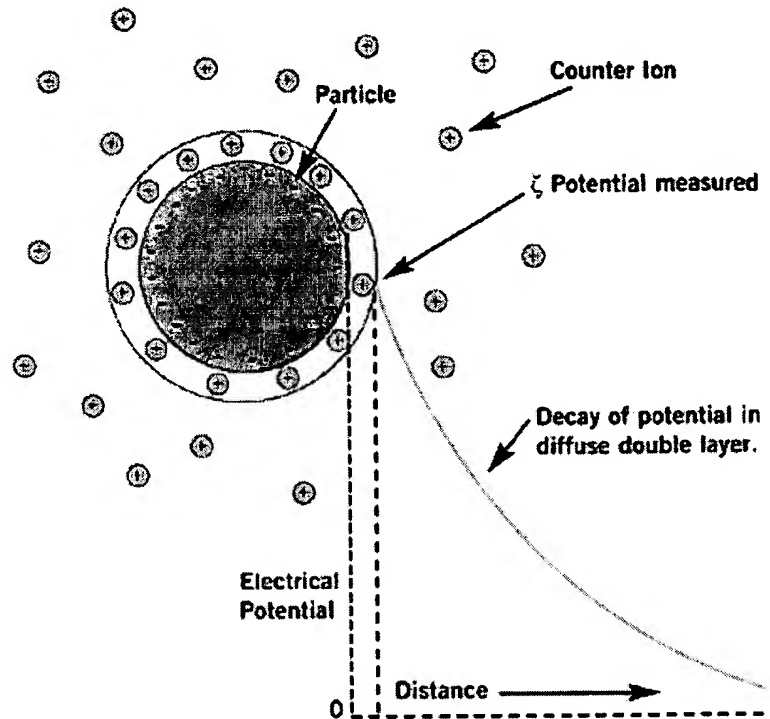


Figure 1. The electrical double layer and the zeta potential.

The electrical potential drops off exponentially with distance from the particle and uniform value in the solvent outside the diffuse double layer. The zeta potential is voltage difference between a plane a short distance from the particle surface and solvent beyond the double layer.¹

When two particles come so close that their double layers overlap, they repel each other. The strength of this electrostatic force depends on the zeta potential. If the zeta potential is too small (typically less than about 25 mV in magnitude), the repulsive force won't be enough to overcome the Van der Waals attraction between the particles, and they will agglomerate. The suspension is said to be unstable when this happens. If the suspension is concentrated and unstable, these agglomerates form networks, and the colloid becomes a paste.

A high zeta potential will prevent particle-particle agglomeration and keep the dispersion uniform and free flowing. Therefore, the goal in most formulations is to maximize the zeta potential. This is particularly important when trying to produce high strength ceramic materials.² A review of ceramic dispersion stability and the importance of zeta potential is given by Pugh.³

The Isoelectric Point

The zeta potential depends on the surface charge density and the double layer thickness. The surface charge density, in turn, depends on the concentration of "potential-determining ions" in the

solvent—ions that have a particular affinity for the surface. In many ceramic systems, the H^+ ion is potential-determining, and so the zeta potential depends on pH.

A graph of zeta potential versus pH typically has the shape shown in Figure 2. This data was obtained on a concentrated alumina slurry using the new zeta potential instrument.

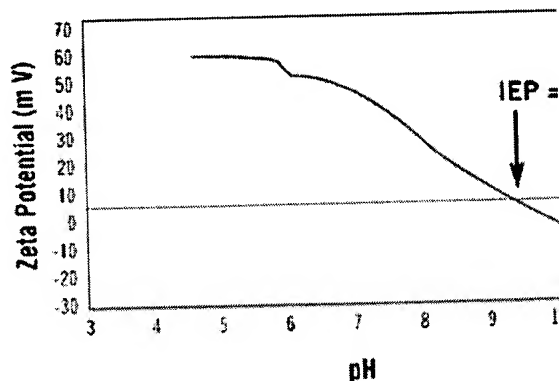


Figure 2. Zeta potential vs. pH for an alumina slurry

The zeta potential is positive for low pH values and negative for high pH values. The point at which the zeta is zero is the isoelectric point (IEP) of the colloid. The IEP is a property of the particle surface. For alumina, the IEP is usually around 9.5. Thus, alumina slurries are usually stable below about pH 8.

Measuring Zeta—The Problem with Dilution

Like most instruments for determining zeta potential, the new instrument measures the particles move in an applied electric field and obtains zeta potential from the velocity of the particles. However, standard devices use optical techniques and are therefore limited to colloids that are diluted enough to allow light to pass through. Typically, this requires concentrations of less than 1/100th of a percent by volume.

Since ceramic slips are made at much higher concentrations, they require very high dilution in order to be measured on the conventional instruments. This dilution is time-consuming, but worse, it can lead to large errors in the zeta potential due to:

- A change in the concentration of the background electrolyte. The suspension must be diluted with an electrolyte that is exactly the same as the electrolyte between the double layers. In a concentrated colloid, that electrolyte concentration can change by the release of ions from the particle surface or by the partial dissolution of colloidal particles—a dissolution that depends on particle concentration.⁴
- Contamination of the particle surface. The diluted sample has such a small particle surface area that the zeta can be altered by trace amounts of surface impurities in the sample.

Measuring Zeta Potential in Concentrates

The new zeta potential instrument avoids these problems by measuring directly on a concentrated colloid, so there is no need for dilution. The reason that the new instrument can measure in the opaque concentrates is that it determines the particle velocity by measuring sound rather than light. In this measurement, the suspension is subjected to a high frequency AC electric field. This causes the particles to jiggle back and forth at the applied frequency because of their electric charge. The particle motion generates ultrasound. The particle velocity is determined by measuring this ultrasound, and the particle zeta potential is determined from this velocity.

This electroacoustic measurement technique, involving the generation of ultrasound and an applied electric field, is called the electrokinetic sonic amplitude (ESA) method.

Note that at these MHz frequencies, the particle velocity depends on its size as well as its zeta potential because of inertia forces. Usually the particle size is not known a priori, but the new instrument accounts for these inertial effects by measuring how the particle velocity

drops off as a function of frequency. Thus, there is no need to enter particle size in instrument, unlike earlier ESA devices.

Applying ESA Measurements to Ceramic Materials

Usually the particle charge in ceramic slips is supplemented by the addition of polyelectrolyte stabilizers such as Dispex A40 or Darvan C. These polymers adsorb to the particle surface and boost the zeta potential. The new zeta potential instrument can be used to determine the optimum amount of dispersant to add.

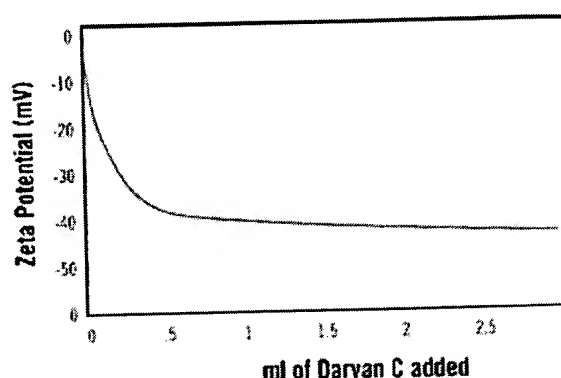


Figure 3. Zeta potential vs. dispersant concentration wt% alumina slurry.

This is illustrated in Figure 3, which shows the change in the zeta potential of alumina particles with the addition of the anionic polymer Darvan C. In this case, the zeta potential has leveled off after about 2.5 ml of polyelectrolyte; there would be no point in adding more Darvan C.

Note that the curve of zeta vs. polyelectrolyte addition depends on factors such as the pH and salt concentration in the solvent. Thus, to completely characterize an additive, it is necessary to make a large number of zeta measurements to examine additions over a broad range of pH and salt concentrations. This would be a daunting task in the standard microelectrophoresis devices, but in the new zeta potential instrument it is straightforward, since the titration process can be completely automated. Figure 4 shows the results of an ESA study of Darvan C addition to an 8 wt% alumina system.⁵

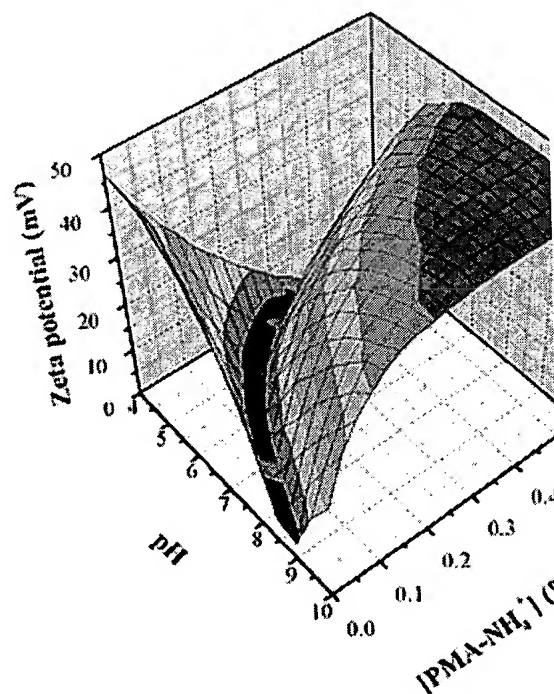


Figure 4. Contour plot of absolute zeta potential as function of pH and Darvan C addition.

Controlling Slip Rheology

As mentioned above, the viscosity increases as the electrical repulsive forces are reduced. Thus, one would expect that the viscosity would be a maximum at the IEP for the ceramic and that the suspension should be free flowing for zeta potential values above about 30 mV.

in magnitude. This has been demonstrated by Johnson et. al.,⁶ who measured a yield stress for an alumina in combination with ESA measurements, and by Greer Bergstrom,⁴ who measured the zeta potential and low shear viscosity of a partially Ce-ZrO₂ system at different levels of polyelectrolyte addition.

In these studies, it was found that the viscosity/yield strength directly correlates to potential. This is to be expected, since zeta is a direct measure of the inter-particle force.

Despite growing appreciation of the importance of the zeta potential in dispersion formulation and material characterization, it has not been used as a standard process parameter because of the inherent difficulties in measurement using the standard devices that require extremely diluted systems. The pH has been used as a defacto potential indicator, since pH was a much easier parameter to measure. However, potential can depend on factors other than pH, particularly in the presence of polydispersing agents.

With the introduction of the new instrument, zeta potential measurements can now cover a wide particle concentration range, without the need for assumptions of the size and particle size distribution. There is no longer any reason to fall back on defacto measurements. The zeta potential is the parameter that needs to be controlled, and can now be directly and easily assessed by using the new instrument.

For More Information

For more information about measuring zeta potential, contact Colloidal Dynamics, St., Building E18, Warwick, RI 02886; (401) 738-5515 ext. 11; fax (401) 738-5542 rman@colloidal-dynamics.com; or visit colloidal-dynamics.com. Colloidal Dynamics also be at Pittcon 2002, booth 3741.

**The ZetaProbe from Colloidal Dynamics*

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- 1 Hunter, R. J., Zeta Potential in Colloid Science, Academic, New York, 1981.
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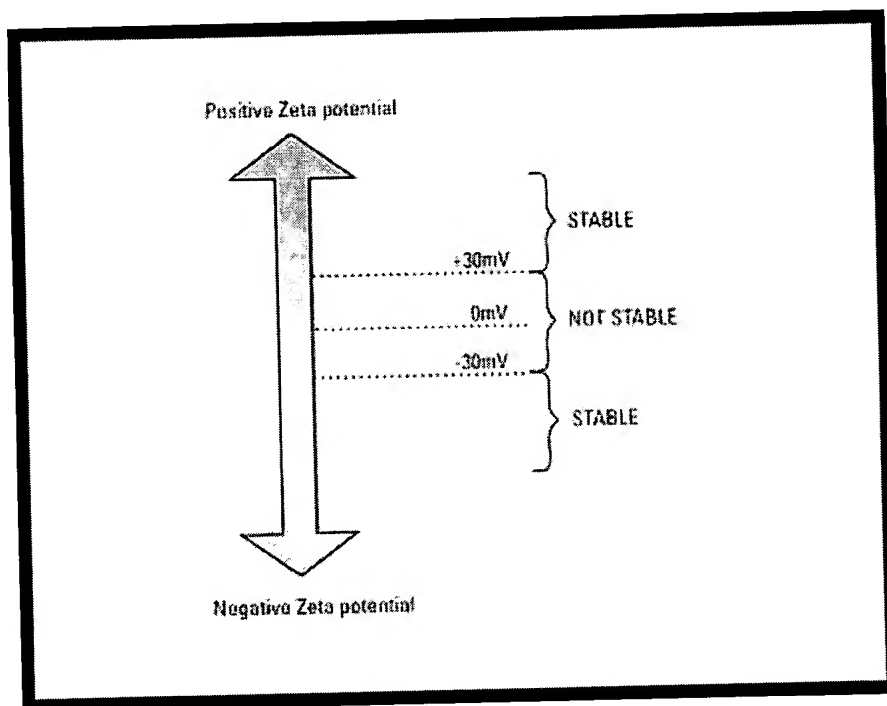
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Zeta Potential

The zeta potential is the overall charge a particle acquires in a specific medium.

- The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system
- If all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability
- If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability
- A dividing line between stable and unstable aqueous dispersions is generally taken at either +30 or -30mV
- Particles with zeta potentials more positive than +30mV are normally considered stable
- Particles with zeta potentials more negative than -30mV are normally considered stable



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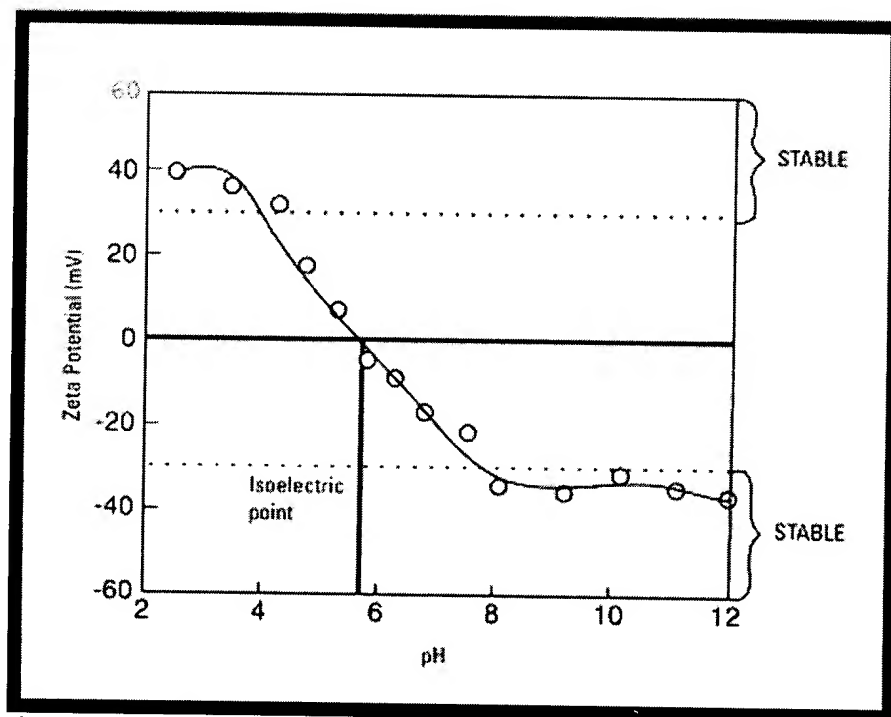
The Influence of Zeta Potential

Zeta Potential and pH

- The most important factor that affects zeta potential is pH
- A zeta potential value quoted without a definition of its environment (pH, ionic strength, concentration of any additives) is a meaningless number

Imagine a particle in suspension with a negative zeta potential

- If more alkali is added to this suspension then the particles tend to acquire more negative charge
- If acid is added to this suspension then a point will be reached where the charge will be neutralized
- Further addition of acid will cause a build up of positive charge
- In general, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH
- There may be a point where the curve passes through zero zeta potential
- This point is called the isoelectric point and is very important from a practical consideration
- It is normally the point where the colloidal system is least stable



In the above example it can be seen that if the dispersion pH is below 4 or above 8 there is sufficient charge to confer stability. However if the pH of the system is between 4 and 8 the dispersion may be unstable. This is most likely to be the case at around pH 6 (the isoelectric point)

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ZetaProbe Applications

Determining the isoelectric point (i.e.p)

The insoluble metal oxides like titania, zirconia, alumina, and silica have a wide variety of uses in ceramics, catalysis, agriculture and many other areas of industry and technology. One of the most significant properties of an insoluble oxide (and of many other materials like the paint pigments) is the **isoelectric point**. The ZetaProbe is the ideal instrument for determining the i.e.p. of such materials.

1 What is the i.e.p. ?

At the isoelectric point of the solid, its zeta potential is zero. That is, however, not sufficient to define the isoelectric point since there are other situations when zeta is zero but the system is not at its i.e.p. For our purposes it suffices to define what is often called the *pristine* i.e.p. which is the point where the clean oxide surface has its zero of zeta potential. This is found by adjusting the pH to the appropriate value. The oxide surface responds by becoming more positive as the pH is lowered by undergoing the following reaction:



If the pH is raised it becomes more negative:



The surface therefore tends to be more negative the higher the pH and more positive the lower the pH. At some intermediate pH, zeta will be zero and that is the i.e.p. These ions which are responsible for generating the surface charge are called the **potential determining ions** for the system. The H^+ and OH^- ions are potential determining ions for oxides and clay minerals and also for proteins and for some other systems as well.

2 Why is the i.e.p. important?

Pure oxides have well defined iso-electric points which can be used to verify the cleanliness of their surfaces. The Table shows the approximate values for some common oxides. The value quoted for silica is approximate because there is some doubt about whether it indeed has an i.e.p. in the accepted sense. The negative surface charge certainly decreases to near zero below pH 3 but it is very

difficult, perhaps impossible, to observe a genuine positive zeta value for this substance in dilute simple salt solutions.

pH of the isoelectric point of various oxides

Oxide	pH of i.e.p.
Silica (SiO_2)	2 - 3
Titania (TiO_2)	5.8
Haematite (Fe_2O_3)	6.5
Alumina (Al_2O_3)	9.1

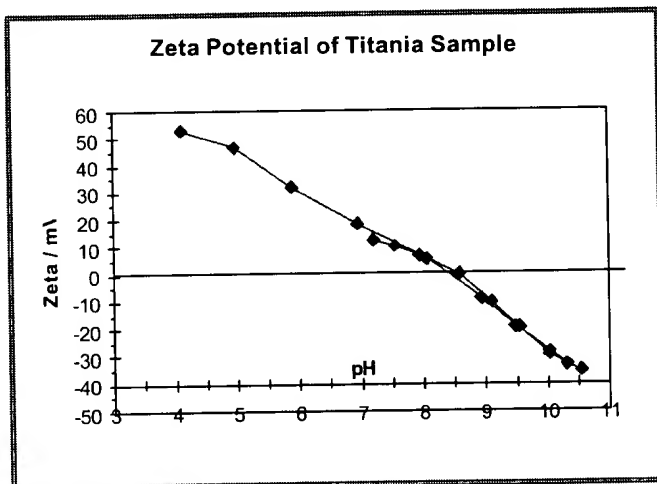
By measuring the i.e.p. of an oxide suspension, which can be very easily done with the ZetaProbe, one can readily verify the cleanliness of its surface. If the particles in a suspension carry an unexpected contaminant it can completely alter the chemical processing behaviour of the suspension.

Although the i.e.p. value for titania is usually quoted as pH 5.8 that value is rarely observed because commercial titania is normally covered with one or more layers of either silica, alumina or zirconia or a combination of those oxides, in order to improve its performance in various situations. The i.e.p. remains an important characteristic of the surface because it helps to identify the coating layer and allows one to easily determine whether a supplier is properly controlling a particular product.

3 Determining the i.e.p. by titration

One must first prepare a suspension which is sufficiently well dispersed to provide a stable zeta potential. One then varies the pH and records the zeta potential over a suitable range. The traditional method of doing this, using microelectrophoresis or light scattering, is extremely tedious. After each pH adjustment one must remove a small sample and dilute it with a suitable solution before measurement. Ideally that diluting solution would have the same pH and salt composition as the suspension and of course that is changing at each step in the titration. If one diluted with a solution of the wrong composition the zeta potential could be quite significantly affected. Not

surprisingly this method often gave rise to unreliable results. Even when the dilution process itself is conducted with great care, the possibility of contamination is always present. Greenwood and Bergstroem [1] give an example of an oxide (Ce-ZrO_2) for which microelectrophoresis gave variable results in this sort of experiment because a component of the oxide itself could dissolve out in the dilution process and alter the result. Their electroacoustic



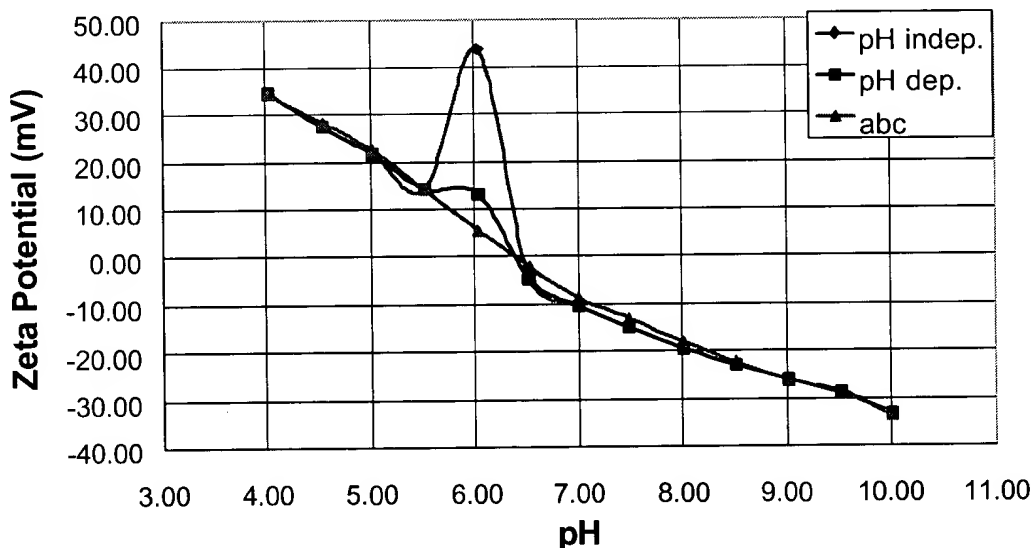
results were much more reliable.

Fortunately that dilution procedure is now a thing of the past. The electroacoustic method allows the measurement to be done on the undiluted suspension with zeta being measured after every addition of acid or base. The figure shows a typical plot of zeta as a function of pH for a titania suspension obtained using electroacoustics. Note the high degree of reproducibility of the results as the i.e.p. is traversed first from below and then from above. The i.e.p. is close to pH 9 suggesting that this titania has an alumina coating. This entire titration can be done in less time than it takes to obtain one or two points by the light scattering or micro-electrophoresis method.

4 Background corrections

The determination of the i.e.p is straightforward when the salt concentration is relatively low (say equal to or less than 10 mM). There are some cases, however, when one wishes to determine the i.e.p as a function of salt concentration and then more care is needed. The problem lies in the fact that the electroacoustic method, which is used in the ZetaProbe, picks up a signal from the background salt as well as the signal from the particles. Normally the salt signal is too weak to affect the results but in the neighbourhood of the i.e.p when zeta is approaching zero that may no longer be the case. If the salt concentration is high enough that signal may be sufficient to disturb the measurement of the i.e.p.

Comparative Background Correction for a 0.1M Zr Dispersion



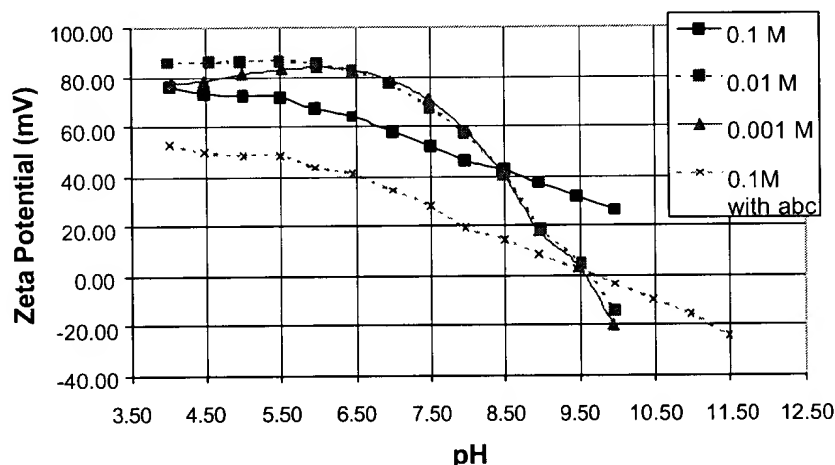
Fortunately we are able to compensate for that effect by using the fact that the signal from the salt has a different form from that of the particles. At the iep there is *only* the salt signal left. The ZetaProbe is able to locate this point and thereby determine the true iep. The ESA signals at the other pH's are then "background corrected" by subtracting the signal at the iep. The

ZetaProbe is the only electroacoustic instrument that can do this automatic background correction.

The above figure shows a comparison of the result obtained on a zirconia dispersion with the ZetaProbe using three different methods to correct for the background salt effect. The curve marked pH indep. is obtained by using a measurement of the salt effect at its natural pH and subtracting that from the signal at all pHs. It gives rise to rather dramatic fluctuations in zeta near the i.e.p. The curve marked pH dep. is obtained by plotting the signal for the background salt over the whole pH range and subtracting that from the suspension signal to estimate zeta. It is obviously an improvement but that still means making two titrations instead of only one. The third and smoothest curve, marked abc, shows the application of the automatic background correction (abc), which does not require any additional measurements. In this case all three methods give concordant results but the manual methods produce fluctuations near the i.e.p which in some cases can lead to significant error especially at higher salt concentrations. Some literature results are in error for that reason.

A rather more striking result is shown by the comparison below

Alumina Dispersions with and without Auto Background Correction



In this figure we show the result for the titration of an alumina sample at low salt (0.001 and 0.01M) without correction and the result at 0.1M with and without automatic background correction. The background corrections at low salt were negligible but at the highest salt concentration there is no accessible i.e.p until one applies the correction and then the agreement with the values at low salt is essentially exact. Accurately determining that i.e.p. by light scattering or microelectrophoresis at 0.1 M salt concentration would be near enough to impossible.

Reference

1. Greenwood, R., and Bergstroem, L. (1997) *J. European Ceram. Soc.* **17**, 537-548.